Review of Corrosion Causes and Corrosion Control In a Technical Facility

T. Charng and F. Lansing

DSN Engineering Section

This report summarizes a general review of causes of corrosion of metals and their alloys. The corrosion mechanism is explained using the concept of electrochemical reaction theory. The causes and methods of controlling of both physicochemical corrosion and biological corrosion are presented in detail. Factors which influence the rate of corrosion are also discussed.

I. Introduction

In a complex facility such as the Deep Space Network, the problems of corrosion and fluid conditioning have been long recognized by engineers and operation and maintenance personnel. A corrosion combatting program influences the economic aspects of the operating equipment; it helps to insure a satisfactory, efficient and continuous operation of the air conditioning system, it lowers power and maintenance costs, and increases equipment life. An extensive review of corrosion causes in metals and alloys and of methods of controlling corrosion and applications of such methods to the DSN environment is required before a successful preventive maintenance program can be started. This report reviews the corrosion field in detail and highlights key areas of concern.

Corrosion is a destructive phenomenon that, besides its economic effects, is detrimental to the appearance of metals and in some cases can cause equipment failure. It occurs in practically all environments (Refs. 1, 2). Corrosion of metals takes several forms. First, an overall surface attack slowly reduces the thickness or the weight of the metal. Second, instead of an overall surface attack, only isolated areas may be affected, producing the familiar localized corrosion. Third, it also occurs along grain boundaries or other lines of weakness because of a difference in resistance to corrosive destruction.

Metals and their alloys tend to enter into chemical union with the elements of a corrosive medium to form stable compounds similar to those found in nature. When metal loss occurs this way, the compound formed is referred to as the corrosion product. Corrosion prevention may involve the use of corrosion-resistant materials, the application of protective coatings, or control of the environment. The selection of materials or methods of protection must be determined for each environmental condition and within prescribed economic limits. Past experience and laboratory testing can serve as a guide in this selection, but exposure under actual conditions is necessary.

Since corrosion is the destruction of metal or alloy by chemical or electrochemical change, it is apparently preceded by a wide variety of mechanisms. Usually this destruction process is associated with the formation of tarnish or oxide films

when directly combined with gases or liquids. The mechanisms of corrosion attack have never been fully understood by researchers in this field. Past experiences have shown several theories to be reasonable, although without complete answers for all types of corrosion. In the literature, it is generally agreed that most corrosion mechanisms involve an electrochemical reaction.

The mechanisms of the galvanic interaction relating the corrosion of ferrous as well as nonferrous metals are discussed in Section II. The various types of metallic corrosion and biological corrosion commonly encountered together with the methods of control or prevention are presented in Sections III and IV, respectively. Physical and chemical factors that affect the corrosion process are discussed in Section V. A summary of the general guidelines on how to combat corrosion is presented at the end of this phase of the review.

II. Corrosion Mechanism

According to electrochemistry, the corrosion reaction can be considered as taking place by two simultaneous reactions: the oxidation of a metal at an anode (a corroded end releasing electrons) and the reduction of a substance at a cathode (a protected end receiving electrons). In order for the reaction to occur, the following conditions must exist:

(1) A chemical potential difference must exist between adjacent sites on a metal surface (or between alloys of a different composition).

(2) An electrolyte must be present to provide solution conductivity and as a source of material to be reduced at the cathode.

(3) An electrical path through the metal or between metals must be available to permit electron flow.

Figure 1 illustrates a typical electrochemical corrosion of iron in contact with water, which is an example case that can be used to describe the electrochemical reactions. In a nearly neutral or slightly acid environment, the water is dissociated into hydrogen ions (H^+) and hydroxyl ions (OH^-) as:

$$H_2O = H^+ + OH^- \tag{1}$$
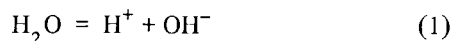
When metal is placed in contact with a liquid, surface ionization occurs because of the electric charge difference at the solid-liquid interface. For example. iron dissolves in water in the form of positively charged ferrous ions (Fe^{++}), where

$$Fe = Fe^{++} + 2e^- \tag{2}$$

Electrochemically, a chemical substance is "oxidized" when it loses electrons to a second substance. The electrode at which oxidation takes place is called "anode." A chemical substance is "reduced" when it acquires electrons. The electrode at which reduction takes place is called "cathode." Hence, oxidation reaction results in the formation of positive charge ferrous ions at the anode. Ferrous ions moving away from the metal surface are further oxidized to ferric ions (Fe^{+++}) as follows:

$$Fe^{++} = Fe^{+++} + e^- \tag{3}$$
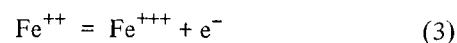
The positively charged ferric ions are attracted to the negatively charged hydroxyl ions and form the corrosion product $Fe(OH)_3$

$$Fe^{+++} + 3(OH)^- = Fe(OH) \tag{4}$$
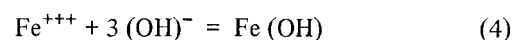
The rust consists of iron hydroxide or iron oxide hydrates in various states, depending on the degree of oxidation and dehydration.

The reduction reaction at the cathode must take place concurrently in order to continue the corrosion process. Several reactions are possible and the one that occurs is determined by the environment. Without the presence of air or oxygen, hydrogen ions can be reduced by the excess of electrons at the cathode surface and evolve as molecular hydrogen by

$$2H^+ + 2e^- = H_2 \tag{5}$$

If hydrogen is not removed from the surface, the cathodic reaction decreases, and the corrosion rate is reduced. With the presence of air, the more likely reaction is the reduction of oxygen. Two possible reactions occur:

$$O_2 + 4H^+ + 4e^- = 2H_2O \tag{6}$$

$$O_2 + 2H_2O + 4e^- = 4(OH)^- \tag{7}$$
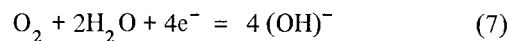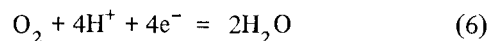
Hydrogen evolution, (Eq. 5), or oxygen reduction with the formation of water, (Eq. 6), is likely to occur in acid media. On the other hand, oxygen reduction with the formation of hydroxyl ions, (Eq. 7), is more dominant in a neutral or alkaline environment. In either case, there is an increase in the alkalinity of the solution at the cathode.

In summary, corrosion occurs when metal atoms detach themselves from the metal surface at the anode and enter the

solution as ions, leaving behind negatively charged electrons in the metal. The electrons flow through the metal to the cathode and neutralize positively charged hydrogen ions that collect at the surface. The neutral hydrogen atoms combine to form hydrogen gas. In solutions where hydrogen tends to evolve too slowly, oxygen is reduced and combines with hydrogen ions or water to form water or hydroxyl ions, respectively.

Corrosion can be attacking the overall surface or be a local phenomenon, depending on the relative proportion of anodic and cathodic areas. When the areas are approximately equal, corrosion is usually uniform over the whole surface. However, when the cathodic area is large compared to the anodic area, the localized attack at anodic sites can be intensified.

Commonly encountered corrosion may be classified into two main groups: physicochemical corrosion and biological corrosion. There are many categories of corrosion in each group. Each is associated with a specific environment. The major types of corrosion attacks, together with the causes and the methods of prevention, are discussed below.

III. Physicochemical Corrosion

The physicochemical corrosion group may be divided into the following seven categories: (a) galvanic corrosion, (b) concentration-cell corrosion, (c) pitting corrosion, (d) intergranular corrosion, (e) stress corrosion, (f) dezincification, and (g) erosion-impingement-cavitation corrosion. Physicochemical corrosion is usually caused by the combination of electrochemical attack, chemical attack, suspended solids or air bubbles, fluid velocity, solution acidity, dissolved salts, temperature, and fabrication. Each category is explained below:

A. Galvanic Corrosion

Galvanic corrosion takes place when the metallic surface is exposed to an aqueous solution which contains some aggressive ionic substances such as $NaCl$, $MgCl_2$, HCl, H_2S, etc.

According to electrochemistry, the galvanic corrosion reaction is caused by an anodic portion and a cathodic portion occurring simultaneously at discrete points on the metallic surface. Flow of electricity from the anodic to the cathodic areas may be generated by local sites either on a single metallic surface because of local point-to-point chemical potential differences on the surface or between dissimilar metals. The driving force to cause galvanic corrosion resulted from a difference in the electromotive force (e.m.f.). The e.m.f. (in volts) can be calculated as,

$$e.m.f. = -\frac{\Delta G}{nF} \qquad (8)$$

where ΔG is the Gibbs free energy of the reaction, n is the number of moles of electrons transferred in the reaction, and F is the Faraday constant (23.06 kcal/(g-mole, volt)).

Table 1 is a list of the galvanic series of metals and alloys (Ref. 3). Metals listed toward the top of the table are more active and therefore anodic to those below; the metal higher in the list will corrode. The magnitude of the electrochemical potential difference of some metals is indicated by their relative position in Table 2. The farther apart metals are in the galvanic series, the greater will be the accelerated corrosion of the least noble metal.

The galvanic corrosion is also affected by other factors such as the distance from the bimetallic junction and the relative areas of two metals. When a bimetallic couple cannot be avoided or the metals insulated from one another, metals should be selected such that they are close to each other in the galvanic series. The smaller of the two metals should be fabricated of the more noble metal.

The anodic and cathodic areas on a metal surface are formed by such variables as inhomogeneities in metal composition, differential surface conditions, metal stresses, or variation in solution concentration as illustrated in Fig. 2. The effects of area on galvanic corrosion are very important. As the ratio of cathode-to-anode area increases, the current density at the anode increases and the cathode is more effectively depolarized. Thus, large cathode areas together with small anode areas should be avoided. Corrosion of the anode in this case may be 100 to 1000 times more than if the two areas were the same.

B. Concentration-Cell Corrosion

This type of localized corrosion is caused by variation in the concentration of environment at various locations on the metal surface such as a deficiency of oxygen, acidity change, buildup of ions, or depletion of an inhibitor. Common forms of this attack are referred to as "oxygen concentration-cell corrosion," or "crevice corrosion." The oxygen concentration cell is an electrolytic cell in which the driving force causing corrosion results from a difference in the amount of oxygen in solution at one point as compared with other locations. Crevice corrosion occurs within or adjacent to a crevice formed by contact with another piece of the same metal, another metal, or with a nonmetallic material.

Concentration-cell corrosion is associated with gaskets, joints, scale, debris, loose protective films, etc. Corrosion

attack is accelerated where the oxygen concentration is least. Metal at the area of low oxygen availability becomes anodic to other areas. Because the cathodic area is large compared to the anodic area, the intensity of attack is usually more severe than on surrounding areas of the same surface.

As mentioned above, in environments where the oxygen concentration is variable, oxygen-derived areas become anodic to oxygen-rich areas. Thus, at the air-water interface in a water tank, fully areated cathodic areas drive the corrosion of deeper, air-deprived areas. The resulting concentration cells can cause corrosion of the steel if the water level stays constant. The oxygen deprivation promotes attack in the anodic areas of the crevices.

However, in equipment handling high sodium chloride concentrate water, crevice corrosion is attributed to the combination of depletion of oxygen and the accumulation of chloride and hydrogen ions in the crevice. As the oxygen in the crevice is depleted, ferrous ions from the corrosion reaction are accumulated, and negatively charged chloride ions must enter the crevice to maintain electrical neutrality. This phenomenon accelerates the following hydrolysis,

$$Fe^{++} (Cl^-)_2 + 2H_2O = Fe(OH)_2 + 2H^+ + 2Cl^- \quad (9)$$
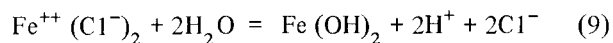
The presence of both H^+ and Cl^- ions accelerates the corrosion attack.

C. Pitting Corrosion

Pitting is generally associated with stagnant pools of liquid. Most pits develop on horizontal steel surfaces and grow downward. Pitting occurs as small areas of localized corrosion which vary in size, frequency of occurrence, and depth. Rapid penetration of the metal may occur, leading to metal perforation. Pitting is generally not a distinctly identifiable problem for steel because the environment that induces pitting also tends to cause a rapid overall corrosion.

Pits are often initiated because of inhomogeneity of the metal surface, deposits or scale on the surface, or breaks in a protective film. These result in the development of cavities or pits. Once a pit is initiated, a concentration-cell is developed since the base of the pit is less accessible to oxygen than is the metal surface.

Halide ions such as chlorides often stimulate pitting corrosion. The mechanism is similar to that described for crevice corrosion. The depletion of oxygen in the pit slows down the generation of hydroxyl ions. The accumulation of positive charges in the form of Fe^{++} then attracts negatively charged chloride ions. The resulting ferrous chloride hydrolyzes to

produce insoluble ferrous hydroxide plus excess hydrogen and chloride ions; both of these ions then accelerate the corrosion at the bottom of the pit.

Inhibitors are sometimes helpful in preventing pitting. Also, a clean, smooth metal surface will be more resistant to pitting.

D. Intergranular Corrosion

Localized corrosion at grain boundaries of the metal or alloy without appreciable attack on the grains or crystals themselves is called intergranular corrosion. It is the result of a difference in potential between anodic grain boundaries and the grains. When severe, this attack causes a loss of strength and ductility to the extent that the metal is actually destroyed by corrosion.

Intergranular corrosion can result in complete metal failure even though only a small portion of the metal is affected. This type of corrosion on stainless steel and some aluminum-copper alloys is thought to be the result of improper heat treatment which causes the precipitation of intergranular compounds. The most effective means of prevention is the proper selection of alloy and/or suitable heat treatment.

E. Stress Corrosion

This form of corrosion can be accelerated by either residual internal stress in the metal or externally applied stress. Internal stress may be produced by nonuniform deformation during cold working (bending, shearing, punching, etc.), by unequal cooling from high temperature, and by internal structure rearrangements involving volume change. Stress induced by rivets and bolts, and by press and shrink fits can also be classified as internal stresses. Stress may simply affect the corrosion behavior of the metal and, if combined with an electrochemical reaction, will produce cracks at an accelerated rate.

Cyclic or repeated stress results in a fatigue failure which is accelerated by corrosion attack. The time required to produce stress-corrosion cracking varies from minutes to years. The severity of stress corrosion for a given material depends, in part, on the degree of stress concentration and the nature of environment and temperature. Typical examples are: cracking of cold formed brass in ammonia environments, cracking of austenitic stainless steel in the presence of chlorides, cracking of monel in hydrofluosilicic acids, and the caustic embrittlement of steel.

Some instances of caustic embrittlement took place in steam boilers made from carbon steel. Sodium hydroxide added for water treatment became concentrated around the welding where there are residual tensile stresses from the

welding operation. The combination effect initiated numerous fine cracks and led to material failure and explosion.

The stress-corrosion cracking can best be avoided by using appropriate heat treatment, selecting the proper alloy for a given environment, putting the equipment in service in a stress free condition, or using suitable protective coatings. Stresses developed during fabrication, particularly during welding, are frequently the main sources of trouble; stress-relieving or annealing should always be considered.

F. Dezincification

Dezincification is recognized by the formation of a pronounced copper color, rather than the yellow color of brass, of copper-zinc alloys. The corrosion may occur as plug filling pits or as continuous layers surrounding an unattacked core of brass. The plug-type dezincification occurs more frequently on low-zinc brasses and the uniform type on high-zinc brasses. The mechanism may involve selective removal of zinc, leaving the copper behind, or dissolution of the alloy followed by redeposition of the copper from the corrosion products.

The tendency to dezincification can be reduced by the addition of small amounts of arsenic, antimony, or phosphorous to the alloy. Rate of attack generally increases with an increase in temperature, increase in solution conductivity, or decrease in solution flow.

This category of corrosion is similar to graphitization of cast iron where iron is removed, leaving a graphite mass with a porous structure. Also, similar types of corrosion have been observed for other alloys, and the tendency is to identify them by similar nomenclature, e.g., dealuminumification, denickelification, etc.

G. Erosion-Impingement-Cavitation

Erosion is the destruction of a metal by the combined action of corrosion and abrasion or attrition resulting from the flow of liquid or gas. When the fluid contains solid particles that are harder than the metal surface affected, erosion will occur by the combined action of corrosion and abrasion. When the fluid does not contain suspended solids, or contains particles that are softer than the metal, erosion will be by corrosion and attrition. Visual evidence of such attack usually takes the form of directional grooves, gullies, waves, rounded holes, or valleys.

Impingement attack is corrosion associated with turbulent flow of a liquid such as at the entrance of a condenser tube or around bends in a pipeline. The high velocity impingement of a liquid can strip away the metal surface's protective film. Solids and gas bubbles can aggravate impingement attack.

Air bubbles in a liquid stream are especially harmful. Formation of transient voids or vacuum bubbles in a liquid stream passing over a surface is referred to as cavitation. This is often encountered around propellers, in pumps and agitators. Cavitation corrosion is often blamed for the damage resulting from the collapse of such vacuum bubbles. More correctly, this should be called cavitation erosion. When bubbles collapse on a metal surface, there is a severe impact or explosive effect that can cause considerable mechanical damage, and corrosion can be greatly accelerated because of the destruction of protective films.

Harder materials, lower velocity, streamlined flowpaths, extra thickness for vulnerable areas, or replaceable impingement plates are general methods used to avert equipment failures due to erosion-impingement attack.

IV. Biological Corrosion

Fungi, algae, and bacteria are the major three causes of biological corrosion which can cause rapid and severe wood rot and metal corrosion. Some important types of these harmful organisms together with methods of prevention and/or control (Refs. 4, 5) are reviewed as follows:

A. Fungi

Fungi are yeasts and molds. Fungal growths are found on cooling-tower wood, basin walls, and in heat exchangers. In wood decay, the cellulose in wood is consumed by organisms until it loses its strength. Fungi are not directly corrosive to metals. However, the deposits of fungi on metal surfaces produce differential concentration cells and interfere with the action of corrosion inhibitors by shielding the metal surfaces from it, causing corrosion. Wood deterioration can be prevented by impregnation with toxic salts that inhibit fungal growth. Fungi can also be controlled by the periodic application of fungicides such as pentachlorophenol salts or tributyl tin compounds. Chlorine is not effective against these organisms.

B. Algae

Algae, like fungi, are relatively large organisms. Algae commonly cause slimy deposits in cooling towers where sunlight and water are present. Deposits of dead algae provide food for bacteria and fungi. Algae are not known to cause corrosion directly, except for occasional occurrences under their deposits. Control can be effected by covering cooling-tower decks to prevent sunlight from reaching the tower water, or with chemicals such as chlorine, quaternary ammonium compounds and copper salts.

C. Bacteria

Bacteria associated with corrosion are of two types: aerobic and anaerobic. Aerobic microorganisms readily grow in an environment containing oxygen, while anaerobic species thrive in an environment virtually devoid of atmospheric oxygen. Each type has a specific action and often is referred to by its effect on materials. Deterioration and corrosion of materials due to the metabolic activity of microorganisms is quite complicated and in some cases not fully understood. Corrosion can be explained by any one or more of the following: (1) producing a corrosive environment, (2) creating electrolytic concentration cells on the metal surface, (3) alternating the surface protecting film, (4) influencing the rate of anodic-cathodic reaction, and (5) changing the environment composition.

Sulfate-reducing bacteria convert water-soluble sulfur compounds to hydrogen sulfide in a slightly acid to alkaline environment. Corrosion of mild steel, stainless steel, and copper alloys is due to conversion of iron to iron sulfide. Nickel and nickel-based alloys are severely pitted under a combination of low pH, sulfides, and reducing conditions. Using chlorine to control the bacteria is not effective because the microorganisms are usually covered by slime masses that prevent the chlorine from reaching the bacteria. In addition, the sulfides surrounding these microorganisms react with chlorine to form chloride salts that negate the effectiveness of chlorine. Special toxicants such as long-chain fatty-acid amine salts and organic-sulfur compounds (for example, methylene bisthiocynate) are effective in controlling these bacteria.

Another group of microorganisms are the nitrifying (or acid-producing) bacteria, which produce nitric acid from ammonia. This results in corrosion of mild steel, copper, and aluminum by chemical corrosion in low pH conditions. These microorganisms are not affected by oxygen and do not neutralize corrosion inhibitors such as chromate or zinc. Chlorine, as well as many nonoxidizing biocides, is very effective in controlling these bacteria. However, with any appreciable amount of ammonia, chlorine may not appear effective; chlorine is neutralized and is unavailable for bacteria control.

A third group of these corrosive microorganisms converts soluble ferrous iron salts into insoluble ferrous oxide. These iron deposits shield metal surfaces from corrosion inhibitors, also promoting corrosion because of concentration-cell. Because the bacteria remove the iron from the area of corrosion, the reaction is accelerated. The iron-depositing bacteria can be controlled with chlorine or many nonoxidizing biocides such as quaternary ammonium compounds.

A fourth group of bacteria feeds on nitrites used as corrosion inhibitors. The growth of this particular group of microorganisms must be kept under control when sodium nitrite inhibitor is used.

Chemical treatment, rather than removal by mechanical cleaning, is a more satisfactory method of combating organisms because of the inaccessibility of corroded areas in some equipment. Fungi and bacteria live in dark areas such as in heat exchangers and piping, as well as in light areas such as in cooling towers or evaporative condensers. If slime and algae are allowed to form an appreciable deposit, it should be removed where practical by mechanical means, and the system should be flushed before chemical treatment.

Chemical treatment using chlorinated phenols, copper sulfate, potassium permanganate, and chlorine has proved to be effective in controlling biological corrosion. Frequently, microorganisms can build up an immunity to a particular algaecide, but not to chlorine. This characteristic makes it necessary to switch to other chemical compounds periodically.

V. Corrosion Parameters

Atmospheric corrosion of carbon steel proceeds at rates up to 0.1 mm per year in environments free of strong chemical splash, spillage or fumes. This corrosion resulted from condensing moisture, sulfur dioxide from fuel combustion, dust bearing corrosives, and the remoteness of structures and equipment from the washing effects of rain water. There is often rapid and severe corrosion that cannot be stopped even when inhibitors are used. Such corrosion may be caused by microbiological organisms. Solution acidity, oxidizing agents, temperature, film deposition, dissolved salts, fluid velocity, and impurities are some of the major corrosion contributors. The seven major corrosion parameters are listed as: (a) solution acidity, (b) oxidizing agents, (c) temperature, (d) films, (e) dissolved salts, (f) fluid velocity, and (g) impurities. Each parameter is explained as follows:

A. Solution Acidity

Solution acidity is represented by the concentration of hydrogen ions with the relation:

$$pH = -\log [H^+] \qquad (10)$$

The tendency for metals to corrode by displacing hydrogen ions from solutions is indicated in the electromotive series such as Table 2 (Ref. 3). Metals above hydrogen in the series displace hydrogen more readily than do those below hydrogen. Whether or not hydrogen evolution will occur is affected by additional factors such as the rate of the corrosion reaction.

Since the discharge of hydrogen ions takes place in most corrosion reactions, acidity of a solution is one of the most important factors in corrosion combatting. A survey of 944 cases involving carbon steel (Ref. 6) showed that 71 cases are related to corrosive acids. As a general rule, acid (pH < 7) solutions are more corrosive than neutral (pH = 7) solutions or alkaline (pH > 7) solutions. In the case of ordinary iron or steel, the dividing line between rapid corrosion in neutral or alkaline solutions occurs at about pH = 4.5 (Refs. 2, 10). For example, Fig. 3 shows the corrosion rate of carbon steel in low-velocity room-temperature water with pH range 4 to 10 is about 0.3 mm per year. In the acidic environment (HCl addition) whereof pH = 2.9, the corrosion rate is above 0.8 mm per year. In an alkaline environment (pH > 10), the corrosion of carbon steel is below 0.3 mm per year. Exceptions are the amphoteric metals such as aluminum and zinc in highly alkaline solutions which cause even more corrosion than acid solutions.

B. Oxidizing Agents

In some corrosion processes, such as the solution of zinc in hydrochloric acid, hydrogen evolves as gas. In the solution of copper in sodium chloride, the removal of hydrogen is effected by a reaction between hydrogen and some oxidizing chemical, such as oxygen, to form water. For this reason, oxidizing agents are often powerful accelerators of corrosion. In many cases, the oxidizing power of a solution is its most important single property.

Oxidizing agents may accelerate the corrosion of one class of materials and retard the corrosion of another class. In the latter case, the behavior of the material usually represents the surface formation of oxides or layers of absorbed oxygen which make the material more resistant to further chemical attacks. This property of chromium is responsible for the principal corrosion-resisting characteristics of stainless steels.

At room temperature, the corrosion rates of carbon steel in a slowly moving, air-saturated (dissolved oxygen 6 ml/l) water containing 165 parts per million (ppm) of $CaCl_2$ range between a negligible amount to about 0.5 mm per year (Ref. 7). The corrosion rate is almost linearly proportional to the concentration of dissolved oxygen. The effect of oxygen concentration on the corrosion of carbon steel in slowly moving distilled water at 25°C is shown in Fig. 4. As indicated in Fig. 4, the corrosion rate decreases as the oxygen level is raised from 12 to 25 ml/l. This is due to passivation formation of a protective oxide film or the chemisorption of excess oxygen on iron. However, the decrease in corrosion rate at high oxygen content will not occur with the presence of appreciable chloride content. The protective film breaks down locally in the presence of chloride. Also, oxygen-lean areas occurring in crevices cannot be protected.

Destructive effects of high oxygen levels may justify deaeration to lessen the rate of corrosion. In general, the expected rate of attack for air-saturated water at low fluid velocities and ambient temperature is about 0.3 mm per year.

C. Temperature

Rate of corrosion tends to increase with rising temperature. Higher temperatures accelerate the diffusion of oxygen through cathodic layers of protective oxide film. Temperature also has a secondary effect through its influence on the solubility of air (or oxygen).

Experimental results indicate that a temperature rise of 18 to 20°C will double the corrosion rate (Ref. 8). Figure 5 presents the influence of temperature on corrosion of iron in water containing dissolved oxygen (Ref. 9). In a closed system where the oxygen cannot escape the corrosion rate increases with temperature until all of the oxygen is consumed. In an open system where the oxygen is free to escape the corrosion rate increases with temperature up to about 80°C. Further increase in temperature results in a marked decrease in corrosion. This is due to a drop in the oxygen solubility in water above 80°C. On the other hand, the corrosion rate of stainless steels will increase considerably through the loss of the oxidizing substance (dissolved oxygen) which is essential to maintain its protective film.

D. Films

There are films of metal oxide, oil and grease that may protect a material from direct contact with corrosive substances. Such oil films may be applied intentionally or may occur naturally as in the case of metals submerged in sewage or equipment used for the processing of oily substances. Once corrosion starts, its further progress often is controlled by the nature of films that may form or accumulate on the metallic surface. One common example is the $PbSO_4$ film on the lead container in contact with sulfuric acid. Another example is the thin oxide film that forms on stainless steel surface.

Insoluble corrosion products may be completely impervious to the corroding environment, hence completely protective, or they may be permeable and allow local or general corrosion to proceed unhindered. Nonuniform or discontinuous film may tend to localize corrosion at certain points by initiating electrolytic effects of the concentration-cell type. Films may tend to retain or absorb moisture and thus, by delaying the time of drying, increase the extent of corrosion resulting from exposure to the atmosphere or to corrosive vapors. It is generally agreed that the rust films formed on low-alloyed steels are more protective than those formed on unalloyed steels.

E. Dissolved Salts

A survey of 180 inorganic salt-aqueous systems (Ref. 6) has indicated that 51% of the salts are corrosive to carbon steel at rates greater than 1.3 mm per year. Acid salts, such as aluminum chloride, ferrous chloride, ammonium chloride, etc., hydrolyze to form acid solutions. Acid salts have a low pH, which will accelerate corrosion simply because of their acidic effect.

Alkaline salts hydrolyze to increase solution pH that may sometimes act as corrosion inhibitors. Examples of these salts are trisodium phosphate, sodium tetraborate, sodium silicate, and sodium carbonate.

Oxidizing salts such as ferric chloride, cupric chloride, and sodium hypochlorite are especially corrosive to carbon steel. Examples of oxidizing salts that are inhibitors include Na_2CrO_4, $NaNO_2$, and $KMnO_4$.

Hard water is less corrosive than soft water. Deposition of calcium carbonate provides a protective film which retards corrosion by shielding oxygen from the cathodic areas. However, protection by $CaCO_3$ precipitation may prove undesirable or unfeasible, since it can clog equipment or reduce heat transfer.

In summary, the presence of acid or neutral salts may increase corrosion rate; whereas the presence of alkaline salts may decrease the corrosion rate.

F. Fluid Velocity

An increase in the relative velocity between a corrosive fluid and a metallic surface tends to accelerate the corrosion rate. This effect is due to the higher rate at which corrosive chemicals, including oxidizing substances such as air, are brought to the corroding surface. Whereas, corrosion resistance results from the accumulation of layers of insoluble corrosion products on the metallic surface, the effect of high velocity may be either to prevent their normal formation, or to remove them after they are formed. The higher the velocity, the thinner will be the films through which corroding substances must penetrate, and through which soluble corrosion products must diffuse. Either effect allows corrosion to proceed unhindered. Similar effects are associated with cavitation-erosion corrosion.

Corrosion rate influenced by fluid velocity occurs frequently in small-diameter tubes or pipes at high velocity such as in condenser and evaporation tubes, in the vicinity of bends and contraction of pipelines, on propellers of agitators, and in centrifugal pumps.

Velocity effects on corrosion rate of carbon steel in natural water, as shown in Fig. 6, can be divided into four ranges according to the velocity magnitude (Ref. 6):

(1) Slight motion (less than 0.3 m/sec) may stop localized attack such as pitting.

(2) At about 0.3 m/sec, the flow may increase the oxygen supply to a level that raises the corrosion rate to as much as 1.0 mm per year.

(3) At a velocity range from 2.4 to 3.0 m/sec, corrosion rate will be about 0.3 to 0.8 mm per year, depending on the surface roughness.

(4) At velocities over 4.5 m/sec, turbulence may greatly accelerate the corrosion rate up to 5 mm per year.

G. Impurities

Impurities in a corrodent can be good or bad. The chloride ion is a good example; the presence of a small amount of chloride in a fluid can break down the passive oxide film on stainless steels. Some impurities may act as inhibitors to retard corrosion. For instance, inorganic oxidizers such as chromates are used as a corrosion inhibitor in cooling water systems. However, if the impurity is removed, a marked increase in corrosion rates may result.

The effects of impurities are varied and complex. One should be aware of the type, quantity, causes, and location before implementation.

VI. Summary

Several ways to prevent or retard corrosion on equipment are reviewed and discussed for their importance in assuring proper engineering function, contributing to extended service life, maintaining appearance, and saving operation and maintenance costs. The "best" method to avoid corrosion is the proper choice of materials that are inert toward the fluids handled and the environment. A knowledge of the reactions, characteristics and general behavior of materials when exposed to certain environments is essential. Obtaining reliable field corrosion data and service history is highly valuable in support of an accurate analysis and satisfactory material and method selection for long equipment life. In the absence of actual corrosion information for a given application, information on other similar applications could be used as a starting point. Materials selected should be further studied in the real system under actual operating conditions.

Corrosion allowances should be considered in the design stage of all new equipment; therefore, it is important that

corrosion rates be determined as accurately as possible. Corrosion influences the choice of materials in design. If the corrosion rate is high, higher alloyed materials, though more expensive, might be more economic. In addition to selecting the proper material of construction, other ways or methods to reduce or prevent corrosion are:

(1) Protective paints.

(2) Protective metal or organic coatings.

(3) Protective films produced on surfaces by chemical reactions.

(4) Control of aqueous solution pH values toward slightly alkaline.

(5) Application of electric potential to equipment.

The choice of cost-effective corrosion-prevention methods is greatly influenced by the interior environment and the exterior equipment environment such as moisture content, sunlight, outdoor temperature, chemical reaction, salt, galvanic reaction, wear, abrasion, and stress. The key to successful corrosion control is the thorough understanding of its causes. Corrosive environment, service conditions, economics and life expectancy of the equipment should be investigated. As the environmental conditions become more severe, or as the standard of acceptability is elevated, changes to higher grade construction material are dictated. Additional work in this area is now being pursued and will be the subject of a follow-on report.

References

1. Fontana, M. G., and Greene, N. D., *Corrosion Engineering*, McGraw-Hill Book Co., New York, 1967.

2. Uhlig, H. H., *Corrosion and Corrosion Control*, 2nd. ed., John Wiley & Sons, New York, 1971.

3. Perry, R. H., and Chilton, C. H., *Chemical Engineers' Handbook*, 5th ed., McGraw-Hill Book Co., New York, 1973.

4. *System Design Manual, Part 5, Water Conditioning*, Carrier Air Conditioning Company, 1972.

5. Puckorius, P. R., "Controlling Corrosive Microorganisms in Cooling-Water Systems," *Chem. Eng.*, Oct. 1978, p. 171.

6. *Corrosion Data Survey – Metals Sections*, 5th ed., National Association of Corrosion Engineers, Houston, Texas, 1974.

7. Uhlig, H. H., Triadis, D. N., and Stern, M., "Effect of Oxygen, Chlorides, and Calcium Ion on Corrosion Inhibition of Iron by Polyphosphates," *J. Electrochem. Soc.*, Feb. 1955. p. 59.

8. Kirby, G. N., "Corrosion Performance of Carbon Steel," *Chem. Eng.*, Mar. 1979, p. 72.

9. Speller, F. N., *Corrosion, Causes and Prevention*, McGraw-Hill Book Co., New York, 1951.

10. Leckie, H. P., "Iron, Carbon Steel, and Low-Alloy Steels in the Process Industries," *Process Industries Corrosion*, National Association of Corrosion Engineers, Houston, Texas, 1975.

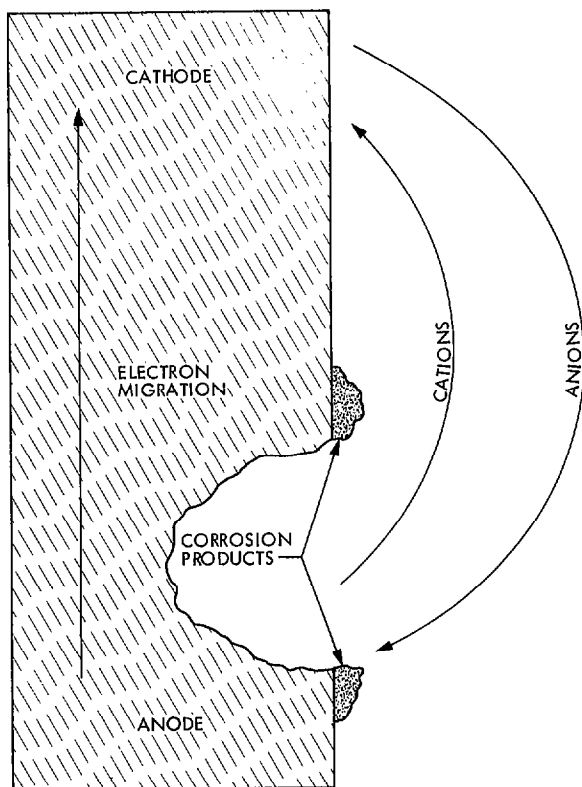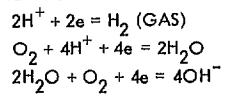**Table 1. Galvanic series of metals and alloys**

Corroded end (anodic, or least noble)

Magnesium
Magnesium alloys
Zinc
Galvanized steel or galvanized wrought iron
Aluminum 6053
Aluminum 3003
Aluminum 2024
Aluminum
Alclada
Cadmium
Mild steel
Wrought iron
Cast iron
Ni-Resist
13% chromium stainless (active)
50-50 lead-tin solder
18-8 stainless type 304 (active)
18-8-3 stainless type 316 (active)
Lead
Tin
Muntz metal
Naval brass
Nickel (active)
Inconel (active)
Monel (active)
Yellow brass
Admiralty brass
Aluminum bronze
70-30 cupronickel
Nickel (passive)
Inconel (passive)
Monel (passive)
18-8 stainless type 304 (passive)
18-8-3 stainless type 316 (passive)
Silver
Titanium
Graphite
Gold
Platinum

Protected end (cathodic, or most noble)

Table 2. Electromotive potential of some metals

Metal	Ion	Molal electroc potential[a] at 25 — Volt
Magnesium	Mg^{++}	−2.34
Aluminum	Al^{+++}	−1.67
Zinc	Zn^{++}	−0.76
Chromium	Cr^{+++}	−0.71
Iron	Fe^{++}	−0.44
Cadmium	Cd^{++}	−0.40
Nickel	Ni^{++}	−0.25
Tin	Sn^{++}	−0.14
Lead	Pb^{++}	−0.13
Hydrogen	H^{+}	Arbitrary zero p
Copper	Cu^{++}	+0.34
Silver	Ag^{+}	+0.80
Palladium	Pd^{++}	+0.83
Mercury	Hg^{++}	+0.85
Platinum	Pt^{++}	+1.20
Gold	Ag^{+++}	+1.42

[a]The potential values given in this table apply only to the conditic where the metal is in contact with a solution in which the activity the ion indicated is 1.0 mol/100 gr water. In any other soluti different values for the potentials would be developed.
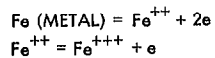
TYPICAL CATHODE REACTIONS:

$$2H^+ + 2e = H_2 \text{ (GAS)}$$
$$O_2 + 4H^+ + 4e = 2H_2O$$
$$2H_2O + O_2 + 4e = 4OH^-$$

TYPICAL ANODE REACTIONS:

$$Fe \text{ (METAL)} = Fe^{++} + 2e$$
$$Fe^{++} = Fe^{+++} + e$$

Fig. 1. Electrolytic corrosion cell

1) 2) – GRAIN DENSITY – THE SMALLER GRAIN No. 2 WILL CORRODE

3 – BOUNDARY – USUALLY CORRODES

6 – INCLUSIONS IN GRAIN

4 – PRECIPITATE IN BOUNDARY (STAINLESS, ETC.)

5 – NOBLE REGIONS IN GRAIN

7 – BREAKS IN PROTECTIVE OXIDE FILMS
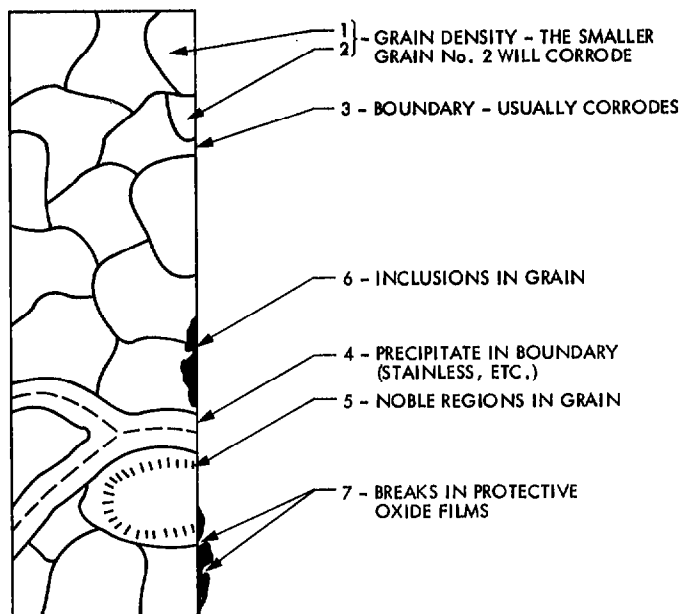
Fig. 2. Grain influence on corrosion

STEEL IMMERSED IN AIR-SATURATE WATER. pH ADJUST BY NaOH OR HCl

40°C

22°C
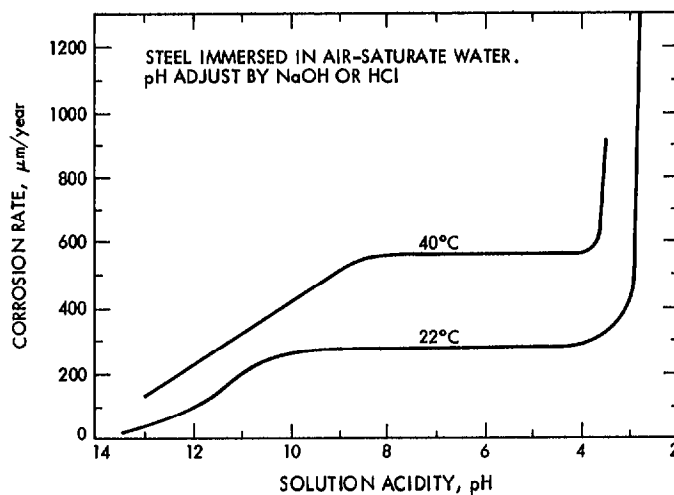
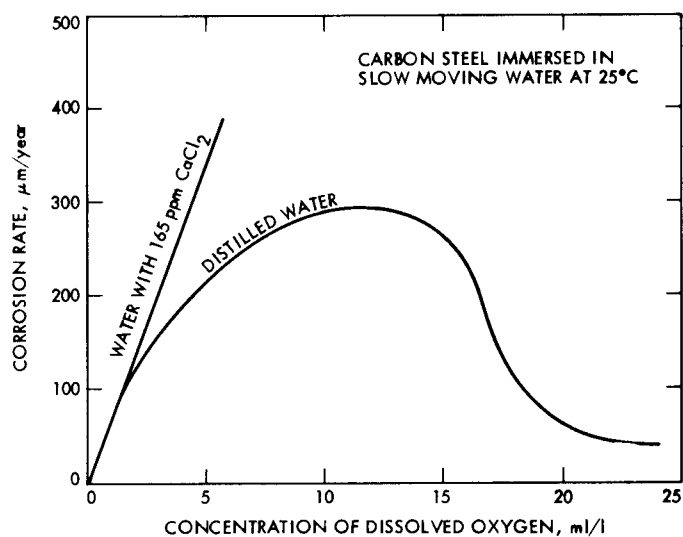**Fig. 3. Effect of solution acidity on corrosion rate**

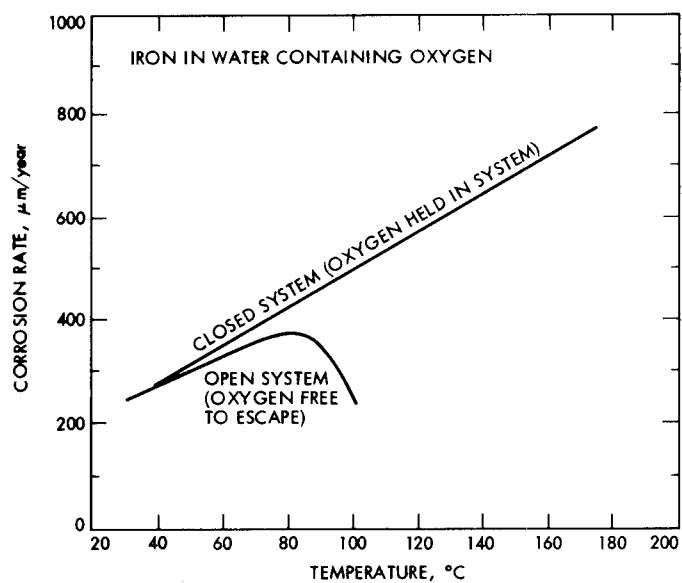**Fig. 4. Effect of dissolved oxygen on corrosion rate**
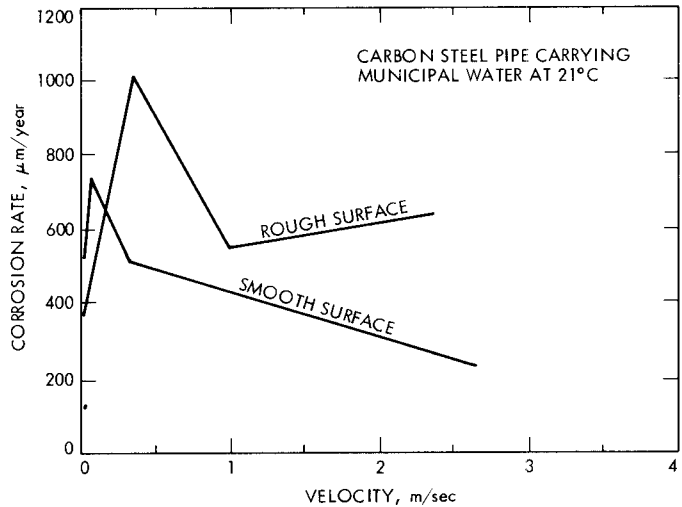

Fig. 5. Effect of temperature on corrosion rate

Fig. 6. Effect of fluid velocity on corrosion rate